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14. ABSTRACT
Electronic structure studies were carried out for chalcopyrite semiconductorswith the aim of modeling their optical properties. The main results of the grant are : a comprehensive study of the intrinsic point defects in ZnGeP2 (including cation antisites, cation and anion vacancies) and CdGeAs2; a study of the feasibility of nonciritical phase matching and associated nonlinear optical parameters in CdSiP2 and CdSiAs2; a study of the band structure of defect chalcopyrites with formula II-III2-VI4; a study of the band gap bowing and its effect on optical parameters in (CuAg)GaS2 and AgGa(Se,Te)2 alloy systems; a study of phonons in ZnGeN2 and ZnSiN2; a study of the electronic band structure in CuS2; a study of the oxygen vacancy in ZnO. The last topic was studied as a means to demonstrate the use of a new computational approach to including band gap corrections in point defect calculations. The before last topic is of relevance to photovoltaic applications.

15. SUBJECT TERMS
semiconductor, nonlinear optics, point defects, chalcopyrite, wide band gap nitrides

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Final Performance Report

Computational Study of Chalcopyrite Semiconductors and Their Non-Linear Optical Properties

Walter R. L. Lambrecht

1 Publications

a. Publications published in peer reviewed journals

1. "Electronic band structure of ordered vacancy defect chalcopyrite compounds with formula II-III_2-VI_4," Xiaoshu Jiang and Walter R. Lambrecht, Phys. Rev. B **69**, 035201 (2004)

2. "Noncritically phase-matched second-harmonic-generation chalcopyrites based on $CdSiAs_2$ and $CdSiP_2$," Walter R. L. Lambrecht and Xiaoshu Jiang, Phys. Rev. B **70**, 045204 (2004)

3. "Theoretical study of cation-related point defects in $ZnGeP_2$," Xiaoshu Jiang, M. S. Miao, and Walter R. Lambrecht, Phys. Rev. B **71**, 205212 (2005).

4. "Structure and phonons of $ZnGeN_2$," Walter R. Lambrecht, Erik Alldredge, and Kwiseon Kim Phys. Rev. B **72**, 155202 (2005)

5. "Theoretical study of the phosphorus vacancy in $ZnGeP_2$," Xiaoshu Jiang, M. S. Miao, and Walter R. Lambrecht Phys. Rev. B **73**, 193203 (2006)

6. "Large band-gap bowing in $Cu_{1-x}Ag_xGaS_2$ chalcopyrite semiconductors and its effect on optical parameters," Chandrima Mitra and Walter R. Lambrecht, Phys. Rev. B **76**, 035207 (2007)

7. "Universal Transition State for High-Pressure Zinc Blende to Rocksalt Phase Transitions," M. S. Miao and Walter R. Lambrecht, Phys. Rev. Lett. **94**, 225501 (2005)

b. Manuscripts submitted to peer reviewed journals but not yet published

1. "First-principles calculation of the zone center phonons in $ZnSiN_2$: comparison with infrared data," Tula R. Paudel and Walter R. L. Lambrecht, Phys. Rev. B (2007), accepted, in press.

2. "Electronic and crystal structure of $Cu_{2-x}S$," Pavel Lukashev, Walter R. L. Lambrecht, Takao Kotani and Mark van Schilfgaarde, submitted to Phys. Rev. B (July 2007)

3. "Band gap bowing in $AgGa(Se_{1-x}Te_x)_2$ system and its effect on the second order response coefficient and the refractive index," Chandrima Mitra and Walter R. L. Lambrecht, submitted to Phys. Rev B (July 2007)

4. "First-principles study of the oxygen vacancy in ZnO: self-consistent gap-corrected approach," Tula R. Paudel and Walter R. L. Lambrecht, submitted to Phys. Rev B (August 2007).

c. Publications in conference proceedings

1. "Electronic Structure of Native Point Defects in $ZnGeP_2$," Xiaoshu Jiang, Maosheng Miao and Walter R. L. Lambrecht, in *Progress in Compound Semiconductor Materials, III-Electronic and Optoelectronic Applications*, ed. Daniel J. Friedman, Omar Manasreh, Irina A. Buyanova, Anneli Munkholm, F. Danie Auret, Mat. Res. Soc. Symp. Proc. Vol. 799, Z5.3.1 (2004).

d. Presentations at conferences not published in proceedings

1. "First-principles study of native point defects in $ZnGeP_2$," Xiaoshu Jiang and Walter R. L. Lambrecht, Fall Meeting of the Ohio Section October 17-18, 2003, Case Western Reserve University Cleveland, Ohio, Abstract P.005
http://flux.aps.org/meetings/YR03/OSF03/baps/abs/S10005.html

2. "Point defects and defect complexes in $ZnGeP_2$," Xiaoshu Jiang, Maosheng Miao and Walter R. L. Lambrecht, APS March meeting 2004 (Montreal), abstract K1.037 Bull. Am. Phys. Soc. **49** (2004);
http://flux.aps.org/meetings/YR04/MAR04/baps/abs/S3610037.html

3. "First-principles Calculations Based Desing of Chalcopyrite Semiconductors for Nonlinear Optical frequency Conversion," Walter R. L. Lambrecht, Enabling Photonics Technologies, Great Lakes Photonics Symposium June 7-11, 2004, Cleveland

4. "Electronics structure of simple and complex point defects in $ZnGeP_2$," X. Jiang, M. S. Miao and W. R. L. Lambrecht, Research Showcase 2004, at Case Western Reserve University, April 2, 2004,

5. "Does the zinc vacancy in $ZnGeP_2$ exhibit a Jahn-Teller distortion?" Walter R. L. Lambrecht and Xiaoshu Jiang, APS March Meeting, Los Angeles, March 2005, Bull. Am. Phys. Soc. **50**, abstract P18.00008; http://meetings.aps.org/Meeting/MAR05/Event/23534

6. "Interactions between native point defects in $ZnGeP_2$," Xiaoshu Jiang, M. S. Miao, and Walter R. L. Lambrecht, APS March Meeting, Los Angeles, March 2005, Bull. Am. Phys. Soc. **50** Abstract P18.00005; http://meetings.aps.org/Meeting/MAR05/Event/23530

7. "Electronic bandstructure, crystal structure and phonons of $ZnSiN_2$," Tula R. Paudel and W. R. L. Lambrecht, APS March Meeting, Baltimore 2006, abstract R46.00009, http://meetings.aps.org/Meeting/MAR06/Event/44174

8. "Structural and Electronic Properties of Copper Sulfides," P. Lukashev and W. R. L. Lambrecht, 18th Annual Workshop on Developments in Electronic-Structure Methods, Columbus, OH, 22-25 June 2006

9. "Structure, electronic structure and phonons of Zn-IV-N2 (IV=Si,Ge,Sn)," T. R. Paudel and W. R. L. Lambrecht, poster presented by T. R. Paudel at the summer school on Ab-Initio Simulation of Crystalline Systems 2006, Spokane, WA September 17-22. 2006.

10. "Point defects and nonlinear optics modeling in chalcopyrite semiconductors," Walter R. L. Lambrecht, seminar at National Renewable Energy Laboratory, June 17 2005

11. "Point defects in ZnGeP2," Walter R. L. Lambrecht, Condensed Matter Seminar, February 27, 2006, Department of Physics, Case Western Reserve University

12. "Large band gap bowing in $CuAgGaS_2$ chalcopyrite semiconductors and its effect on optical parameters," C. Mitra and W. R. L. Lambrecht, APS March Meeting, Denver 2007, Bull. Am. Phys. Soc. **52**,

abstract no. D40.00008 (2007);
http://meetings.aps.org/Meeting/MAR07/Event/57971

13. "Crystal and Electronic Structure of Copper Sulfides," P. Lukashev and W. R. L. Lambrecht, APS March Meeting, Denver 2007, Bull. Am. Phys. Soc. **52**, abstract no.H41.00013 (2007);
http://meetings.aps.org/Meeting/MAR07/Event/58515

14. "Electronic structure of the oxygen vacancy in ZnO including a self-consistent band-gap corrected approach," Walter R. L. Lambrecht and T. R. Paudel, to be presented at the MRS Fall Meeting 2007 in Symposium L: ZnO and Related Materials, abstract L4.2.

15. "Phonons in Zn-IV-N2 semiconductors," T. R. Paudel and W. R. L. Lambrecht, to be presented at the MRS Fall Meeting 2007 in Symposium Q: Nitrides and Related Bulk Materials, abstract Q1.9.

16. "Raman Spectroscopy of Single Crystal $ZnGeN_2$," Timothy Peshek, Kathleen Kash, John C. Angus, Tula R. Paudel and Walter R. L. Lambrecht, to be presented at the MRS Fall Meeting 2007 in Symposium Q: Nitrides and Related Bulk Materials, abstract. Q1.1

e. Manuscripts in preparation to be submitted to peer reviewed journals

1. "Jahn-Teller distortion of the zinc vacancy in $ZnGeP_2$," Xiaoshu Jiang and Walter R. L. Lambrecht, in preparation

2. "Native point defects in $CdGeAs_2$," Tula R. Paudel and Walter R. L. Lambrecht, in preparation

f. Theses

1. "First principles study of electronic structures of defects in ZnGeP2 and defect chalcopyrites," Xiaoshu Jiang, Ph. D. Thesis, Case Western Reserve University (2005), available from Kelvin Smith Library.

2. "Crystal and electronic structure of copper sulfides", Pavel Lukashev. Ph. D. Thesis, Case Western Reserve University (2006), available from Kelvin Smith Library and in electronic form:
http://www.ohiolink.edu/etd/view.cgi?acc

Summary

a. Number of published papers in peer reviewed journals: 7

b. Number of submitted (not yet published) papers to peer reviewed journals: 4
c. Number of conference proceedings published: 1
d. Number of presentations at conferences, seminars, not published: 16
e. Number of manuscripts in preparation (not yet submitted): 2
f. Number of theses completed: 2

2 Summary data on human resources

The following scientists were involved with the project:

- Walter R. L. Lambrecht, Principal Investigator, Professor of Physics
- Maosheng Miao, postdoctoral Sr. Research Associate (part time, 2002-2006)
- Xiaoshu Jiang, graduate student (full time, completed Ph.D, 2002-2005)
- Pavel Lukashev, graduate student (part time, completed Ph.D, 2005-2006)
- Tula Ram Paudel, graduate student (part time, Ph.D. in progress, 2005-2007)
- Chandrima Mitra, graduate student (part time, Ph.D. in progress, 2005-2007)

a. Number of Scientists supported by this agreement: 6
b. Number of Graduate Students supported by this agreement: 4
c. Number of Post Doctoral Associates supported by this agreement: 1
d. Number of Faculty supported by this agreement: 1
e. Number of Other Staff supported by this agreement: 0
f. Number of Undergrads supported by this agreement: 0
g. Number of PhD(s) awarded as a result of this agreement: 2
h. Number of Bachelors Degrees awarded as a result of this agreement: 0
i. Number of Master Degrees awarded as a result of this agreement: 0
j. Number of FTE graduate students supported per year: 1
k. Number of FTE postdoctoral associates supported per year: 1
l. Faculty summer salary support in months per year: 1

3 Report of Inventions

a. Number of inventions or discoveries disclosed to University Office of Sponsored Research: 1
Title: Materials that allow for non-critical phasematching in second order nonlinear optical frequency conversion
Date of disclosure: September 14, 2007.
b. Number of Patents Sumbitted as a result of this agreement: 0
c. Number of Patents Awarded as a result of this agreement: 0

4 Narrative Description of Scientific Accomplishments

The main goals of the project were to study: (1) the physics of point defects in chalcopyrite semiconductors that have currently applications in nonlinear optics, such as $ZnGeP_2$ and $CdGeAs_2$; (2) the properties of ternary alloys among different chalcopyrites to evaluate the dependence of optical properties on the composition of the materials; (3) understand the trends in the family of chalcopyrite semicondutors and related materials with the aim to identify potential materials with favorable combinations of properties for non-linear optical applicsations.

The methodology followed in the work is based generally on density functional theory first-principles calculations. We use the full-potential linearized muffin-tin orbital method to solve the Kohn-Sham equations in the local density approximation (LDA). Defects are modeled with supercells (i.e. peridodic boundary conditions). Alloy problems, in particular the disorder aspect, were tackled with the use of so-called special quasirandom structures (SQS). Several aspects of the methodology were refined during the course of the project. For example, early on, we had to include the use of a uniform background compensating charge density in the codes in order to allow us to deal with charged point defects. The issue of size dependence in such calculations, and so-called Makov-Payne monopole and quadrupole correctons were studied. We also demonstrated the use of shift potential to address the LDA band gap problem in point defect studies and ultimately showed how this problem can be more consistently be addressed by a novel implementation of the LDA+U approach. Thus, several improvements in methodology resulted from this work.

The following tasks were accomplished and led to the publications iden-

tified below.

- A study was carried out of the cation antisite defects Zn_{Ge}, Ge_{Zn}, cation vacncies V_{Zn}, V_{Ge} and anion vacancies V_P in $ZnGeP_2$ and some complexes among these defects and resulted in 3 publications [1, 2, 3] and a major portion of the Ph. D. thesis of Xiaoshu Jiang.

- A further in-depth study was carried of the possibility of a Jahn-Teller distortion of the V_{Zn} defect. While a possible mechanism which could explain the associated experimental (electron paramagnetic resonance and electron nuclear douuble resonance) EPR-ENDOR data was identified,[4] some technical problems remain associated with this problem. The currently available level of theory, which is based on the local density approximation (LDA), does not find the proposed Jahn-Teller distortion to be energetically favorable. It was found that in part this could be related to the formation of Ge dangling bonds next to the vacancy as a result of using too small a simulation cell but also could be related to the incomplete cancellation of self-interaction effects in LDA. A calculation at the Hartree-Fock level was pursued using cluster models and the Gaussian program but did not lead to a satisfactory explanation of the experimental results. A description of this work is included in the Ph. D. Thesis of Xiaoshu Jiang.

- A similar study was carried out of the point defects in $CdGeAs_2$. Because $CdGeAs_2$ has a negative band gap in the local density approximation, it was essential to develop a band gap correction approach. This was done using the so-called LSDA+U method, which was developed under another project (supported by ONR and NSF) during the period of this grant. The results were only obtained in the last months of the extension period of this project and remain to be fully analyzed and prepared for publication.

- As part of our tests of the LSDA+U approach for dealing with band gap corrections, we applied the method to a recent problem of interest in wide-band-gap semiconductors, namely the oxgygen vacancy in ZnO. For this system, a controversy exists in the literature as to whether the defect levels lie in the uppor or lower half of the band gap, and this discrepancy results purely from different ways of applying band gap corrections. Our new approach sheds new light on this problem. A paper on this work was submitted for publication[5] and the work was also submitted for presentation at the upcoming MRS Fall meeting.

- A study was carried out of the electronic band structures in the family of II-III_2-VI_4 defect chalcopyrites. These are related to I-III-VI_2 chalcopyrites by a doubling of the unit cell and replacing the group-I atoms by a group II atom and a vacancy. These materials have received only little attention in the literature and our work [6] presents the first systematic approach to understanding the trends in their band gaps and other properties.

- In terms of optimizing materials for non-linear optical calculations, we had found in a previous funding period supported by AFOSR, that $AgGaTe_2$ has a twice higher $\chi^{(2)}$ than $AgGaSe_2$, which is currently one of the main optical materials used for frequency conversion because of its very wide window of transparency. Work at WPAFB by Mel Ohmer and coworkers, had also found that $AgGaTe_2$ has a positive instead of negative birefringence. This lead to the idea (which was in fact patented by researchers at WPAFB) that alloys of $AgGa(Se_{1-x}Te_x)_2$ could be designed to have the optimal index of refraction to allow for so-called non-critical phasematching. However, this all rests on the assumption that indices of refraction vary linearly with concentration in the alloy. However, usually semiconductor band gaps show some degree of bowing instead of linear behavior. In turn this can be expected to lead to a nonlinear behavior of the indices of refraction. We thus studied the fundamental question of how the index of refraction and the $\chi^{(2)}$ vary as function of concentration in quaternary alloy systems. We carried out this study for $AgGa(Se_{1-x}Te_x)_2$ in the last months of the project and submitted the results for publication.[7] It was found that in this system the bowing of the index of refraction is only minor, so that previous results based on linear behavior should provide a reasonable estimate.

- Closely related to the previous topic, we also studied the band gap bowing and index of refraction and $\chi^{(2)}$ as function of concentration x in Cu_xAg_{1-x} GaS_2 alloys. For this quaternary alloy family, experimental reports existed of a large band gap bowing. We found that this leads indeed to large bowing of the index of refraction and of $\chi^{(2)}$. An interesting feature of this alloy system is that while Cu-based compounds have smaller gaps than the corresponding Ag-based compounds, they nevertheless have a smaller $\chi^{(2)}$ in defiance of the rule of thumb that smaller gaps lead to higher $\chi^{(2)}$ that is generally observed. In fact, an unexpected result of this work was that the $\chi^{(2)}$ of a 50 %

mixed quaternary $Cu_{0.5}Ag_{0.5}GaS_2$ is predicted by our calculations to have a higher $\chi^{(2)}$ than either of the end compounds. This work was published in [8].

- When comparing the two families of chalcopyrite materials, the II-IV-V_2 family and the I-III-VI_2 family, one generally finds higher $\chi^{(2)}$ and also stronger bonds in the former than in the latter. Stronger bonds are among other expected to lead to higher laser damage thresholds, and are thus important for improving the tolerable input and output power levels of frequency conversion optical devices. On the other hand, the birefringence in most II-IV-V_2 materials is positive, thus precluding so-called non-critical phase matching. This led us to the question: do there exist II-IV-V_2 chalcopyrites with negative birefringence, and if so can they be alloyed to achieve non-critical phasematching? As already outlined in the proposal for this project, we found a correlation between birefringence and c/a ratio of the crystal structure and on this basis anticipated that $CdSiAs_2$ and $CdSiP_2$ would have negative birefringence. We thus embarked on a computational study of these materials. We found indeed that both have negative birefringence by our calculations, and in fact, later found confirmation of this in some little known works in the Russian literature, which was not yet included in the reference compilations on which our original proposal was based. However, when studying in more detail whether non-critical phasematching is possible, for some desirable target frequency conversion processes into the mid infrared range, we found that the birefringence in $CdSiAs_2$ is too small to overcome the index of refraction dispersion between pump and target beam wavelengths. However, our work also suggests that by compressing the c/a ratio, one might make the birefringence more negative. The details of the phasematching angle curves as function of strain were worked out and led to a new proposal for turning $CdSiAs_2$ into a useful nonlinear optical material by applying external uniaxial or biaxial stress. In fact, this concept was ultimately submitted as an invention disclosure. $CdSiP_2$ was found to have stronger negative birefringence, but on the other hand has a less strong $\chi^{(2)}$. So, as usual there is a trade-off. One could tune birefringence by making alloys of the type $CdSi(P_{1-x}As_x)_2$. This work was published in [9]. The practical implementation of these ideas will however take substantial further development of crystal growth techniques and is thus not close to commercial applications.

- Similar to the chalcopyrite family which is based on an ordered arrangement of II and IV cations on the cation sublattice of zincblende, there exists a family based on the wurtzite structure, which occurs naturally for III-nitride materials. These are potentially an interesting family of optoelectronic materials competing with the III-nitrides. We had in the past already studied some of these nitrides but as an exploratory subproject of this grant, we started a study of the lattice vibrations in these materials. We did so mainly because we were aware of the availability of some Raman and infrared data in the literature. During a sabbatical stay in 2005 at NREL, we became familiar with computational methods for calculating phonons in crystals, based on the linear response method and the ABINIT code. This led to a first publication on the phonons in $ZnGeN_2$.[11] In this work however, we could only compare with Raman spectra on polycrystalline powders. Subsequently, we applied the same approach to $ZnSiN_2$ and used it to simulate infrared reflectivity spectra on single crystals. This led to a second publication.[12] We are now trying to find funding for continuing this project in collaboration with an experimentalist in our department who is working on the crystal growth of this family of materials. A joint experimental/computational study was carried out of the Raman spectra of single crystal $ZnGeN_2$ needle type crystals and will be presented at the MRS Fall Meeting in November 2007. (See presentations listed above).

- Chalcopyrite semiconductors of the family $Cu(In,Ga)Se_2$ (CI(G)S) are an attractive material for photovoltaic (PV) solar energy conversion in thin film materials. In part, this is owing to a relatively greater tolerance to lattice defects in these materials. For example, high conductiviy and reduced recombination along grain boundaries is observed in some of these films. This in turn was tentatively related to the nature of the valence band maximum which is Cu-*d* like. This leads to a favorable band-offset for carrier separation at interfaces or surfaces with reduced Cu coordination. However, one of the things that is slowing down the development of these PV materials is the relative scarcity of In. It thus seemed useful to look for other Cu-based compounds without In. We found through literature search that Cu_2S is one of the earliest used solar cell materials but was eventually abandoned because of long-term stability problems. We thought this question was worth re-investigating. Encouraged by the prospective of a possible collaboration with a chemist in our university who was able to syn-

thesize Cu_2S in nanoparticle form, we thus started a study of Cu_2S. It turned out that in spite of its simple chemical composition, its crystal structure is quite complex and theoretical studies of its band structure had never been reported prior to our study. A novel methodology had to be developed to construct suitable models for simulating the random distribution of Cu atoms in this material. Furthermore, it proved important to include corrections beyond LDA. To this end we collaborated with Mark van Schilfgaarde at ASU who provided us with some calculations using his recently developed state-of-the art quasiparticle self-consistent GW method for one of the simpler model structures. We were then able to use this information to apply a correction to the more complex models. Our work on this subject ultimately led to the doctoral thesis of one Ph.D student and one paper submitted to Phys. Rev. B.[10] We also used it as a starting point for proposals to NSF and DOE in which the PV applications of these materials in nanoparticle form would be pursued.

Summary and outlook

All, in all, most of the initially set goals of this project were successfully accomplished. There remains work to be done on point defects in the $AgGaTe_2$ and $AgGaSe_2$ systems and we would be happy to pursue this with future funding from AFOSR if there is a continuing interest in this topic. There also remains work to be done to further refine the computational techniques for dealing with some of the more subtle aspects of defect physics, in particular relating to the partially unresolved problem of the structural relaxation around a V_{Zn} in $ZnGeP_2$ and the associated details of the hyperfine structure measured in magnetic resonance experiments. Similar problems, in fact, plague other known defect systems, although they have not been widely recognized or acknowledged. The project led to several spin-offs into new directions: (1) point defects in ZnO, (2) the fundamental properties of ternary nitrides of the type II-IV-N_2, a new family of wide-band-gap semiconductors, (3) the study of Cu-sulfides and their potential in photovoltaic energy conversion.

5 Interactions

During the course, of the project, we engaged in several collaborations. Our work on the $ZnGeP_2$ point defects was closely related to the EPR-ENDOR studies by the group of Larry Halliburton and Nancy Giles at West-Virginia Univeristy, Morgantown, WV. Our work on $ZnGeN_2$ and related materials,

was initially carried out with researchers at NREL (kwiseon Kim) and is now continued with a collaborator (Kathleen Kash) at CWRU. Our work on Cu_2S was inspired in part by work of a colleague in the Dept. of Chemistry (Clemens Burda) at CWRU. Our work on (Cu,Ag)GaS_2 was inspired by and relevant to experimental work by Prof. Peter Yu at University of California, Berkeley and his collaborators in South Korea.

6 Summary of timeline and financial report

The project stretched over a somewhat unusually long period, from 2002 till 2007. It was initially a 3 year continuation grant for a total of $382,125, following on an earlier related AFOSR project started in 1999 and extended with a no-cost extension till Oct. 2002. The present project was originally scheduled to end on October 14, 2005, but received a no-cost extension till June 2006. In May 2006, a final extension with additional support to the amount of $30,000 was requested and awarded on August 10, 2006 bringing the total to $412,125. The new extension was finally no-cost extended till April 14, 2007. The present final project report was delayed by the desire to first finalize some of the papers, so as to enable us to prepare a more accurate final report representing the final outcomes of the project. The writing of 5 of the reported papers was completed during the summer of 2007, after completion of the offical grant period.

References

[1] "Electronic Structure of Native Point Defects in $ZnGeP_2$," Xiaoshu Jiang, Maosheng Miao and Walter R. L. Lambrecht, in *Progress in Compound Semiconductor Materials, III-Electronic and Optoelectronic Applications*, ed. Daniel J. Friedman, Omar Manasreh, Irina A. Buyanova, Anneli Munkholm, F. Danie Auret, Mat. Res. Soc. Symp. Proc. Vol. 799, Z5.3.1 (2004).

[2] "Theoretical study of cation-related point defects in $ZnGeP_2$," Xiaoshu Jiang, M. S. Miao, and Walter R. Lambrecht, Phys. Rev. B **71**, 205212 (2005).

[3] "Theoretical study of the phosphorus vacancy in $ZnGeP_2$," Xiaoshu Jiang, M. S. Miao, and Walter R. Lambrecht Phys. Rev. B **73**, 193203 (2006)

[4] "Jahn-Teller distortion of the zinc vacancy in $ZnGeP_2$," Xiaoshu Jiang and Walter R. L. Lambrecht, in preparation

[5] "First-principles study of the oxygen vacancy in ZnO: self-consistent gap-corrected approach," Tula R. Paudel and Walter R. L. Lambrecht, submitted to Phys. Rev B (August 2007).

[6] "Electronic band structure of ordered vacancy defect chalcopyrite compounds with formula II-III_2-VI_4," Xiaoshu Jiang and Walter R. Lambrecht, Phys. Rev. B **69**, 035201 (2004)

[7] "Band gap bowing in $AgGa(Se_{1-x}Te_x)_2$ system and its effect on the second order response coefficient and the refractive index," Chandrima Mitra and Walter R. L. Lambrecht, submitted to Phys. Rev B (July 2007)

[8] "Large band-gap bowing in $Cu_{1-x}Ag_xGaS_2$ chalcopyrite semiconductors and its effect on optical parameters," Chandrima Mitra and Walter R. Lambrecht, Phys. Rev. B **76**, 035207 (2007)

[9] "Noncritically phase-matched second-harmonic-generation chalcopyrites based on $CdSiAs_2$ and $CdSiP_2$," Walter R. L. Lambrecht and Xiaoshu Jiang, Phys. Rev. B **70**, 045204 (2004)

[10] "Electronic and crystal structure of $Cu_{2-x}S$," Pavel Lukashev, Walter R. L. Lambrecht, Takao Kotani and Mark van Schilfgaarde, submitted to Phys. Rev. B (July 2007)

[11] "Structure and phonons of $ZnGeN_2$," Walter R. Lambrecht, Erik Alldredge, and Kwiseon Kim Phys. Rev. B **72**, 155202 (2005)

[12] "First-principles calculation of the zone center phonons in $ZnSiN_2$: comparison with infrared data," Tula R. Paudel and Walter R. L. Lambrecht, Phys. Rev. B (2007), accepted, in press.